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Preliminary communication

THE CRYSTAL STRUCTURE OF $[WH_2Cl_2(PMe_2Ph)_4]$ AND ITS DEHYDROCHLORINATION TO GENERATE A REACTIVE METAL CENTRE

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Summary

$[WH_2Cl_2(PMe_2Ph)_4]$ (A) is shown by X-ray analysis to have a dodecahedral structure with *cis*-hydrogen atoms (W—H 1.26(7), 1.46(5) Å, R = 0.032). Complex A easily dehydrochlorinates with base in presence of ligand (L) to give a range of complexes of L (L = CO, N_2, RNC, C_2H_4 etc.).

The di- and poly-hydrides of the Group VI transition metals [1—3] are of potentially high significance with regard to important processes such as nitrogen fixation [4], activation of saturated hydrocarbons etc. [1]. Although a large number of examples of such hydrides has been prepared, it is only relatively recently that their chemistry has been examined in any detail; accurate structural information is also limited.

Here we describe the X-ray structure of the hydride $[WH_2Cl_2(PMe_2Ph)_4]$ (A) which we have recently prepared [5]. We also report on its facile dehydrochlorination by base in presence of a range of ligands: this provides a convenient route to a variety of complexes.

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*X-ray crystal analysis**

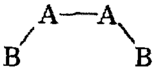
Compound A forms orange, rectangular air-stable prisms from thf/i-PrOH.

Crystal Data: $C_{32}H_{46}Cl_2P_4W$ = 809.4, triclinic, $P\bar{1}$ (No. 2). a 8.169(2), b 9.892(2), c 22.858(4) Å, α 93.25(1), β 90.03(2), γ 112.34(2)°, U 1705.2 $Å^3$, $Z = 2$, D_c 1.58 g cm^{-3}, $F(000) = 812$, μ(Mo-K_α) 38.2 cm^{-1}, λ(Mo-K_α) 0.71069 Å.

During processing of diffractometer data, Lorentz and polarisation factors and corrections for absorption and slight crystal deterioration were applied. The structure was solved by the heavy atom method using 6666 independent reflections with positive net intensities.

The two hydride atoms were located in difference maps and allowed to refine independently in the final cycles of the least-squares refinement. At convergence, $R = 0.032$ and $R' = 0.033$.

Description of the structure

Two views of the complex molecule are in Fig. 1 and 2, and the W-atom is seen to have approximately dodecahedral eight-fold coordination. In the two  planes of coordinating atoms, viz. P(4)—H(1)—H(2)—P(6) and P(3)—Cl(1)—Cl(2)—P(5), these planes intersect at right angles to form the dodecahedron, the B position are all occupied by the P-atoms; in one plane, the two A's are hydrido groups and, on the opposite side of the complex, the two chloro groups are *cis*. The pseudo-two-fold axis which relates the coor-

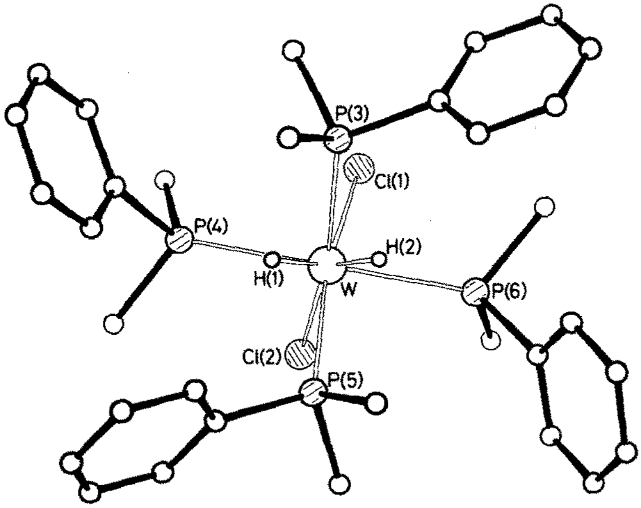


Fig. 1. The complex $[WCl_2H_2(PMe_2Ph)_4]$ (A), viewed along the pseudo-two-fold axis of symmetry. Coordination distances (with e.s.d.s in parentheses) are: W—H(1) 1.26(7), W—H(2) 1.46(5), W—P(3) 2.457(1), W—P(4) 2.531(1), W—P(5) 2.468(1), W—P(6) 2.548(1), W—Cl(1) 2.533(1), W—Cl(2) 2.528(1) Å; H(1)—W—H(2) 78(3), Cl(1)—W—Cl(2) 79.9(1)°.

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*Atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain. Any request should be accompanied by a full litertaure citation for this communication.

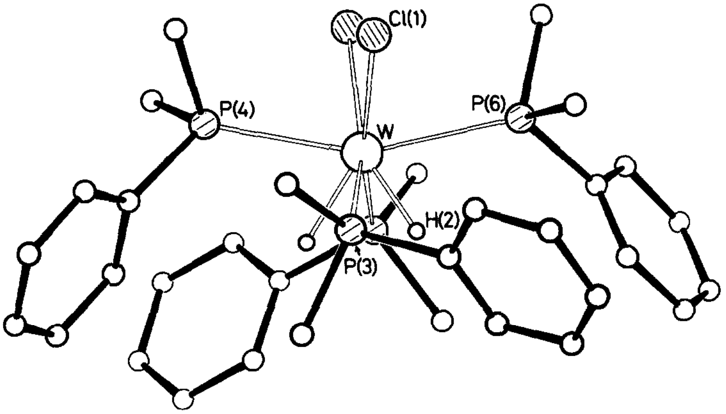


Fig. 2. View of complex A, with the pseudo-two-fold axis vertical in the plane of the paper.

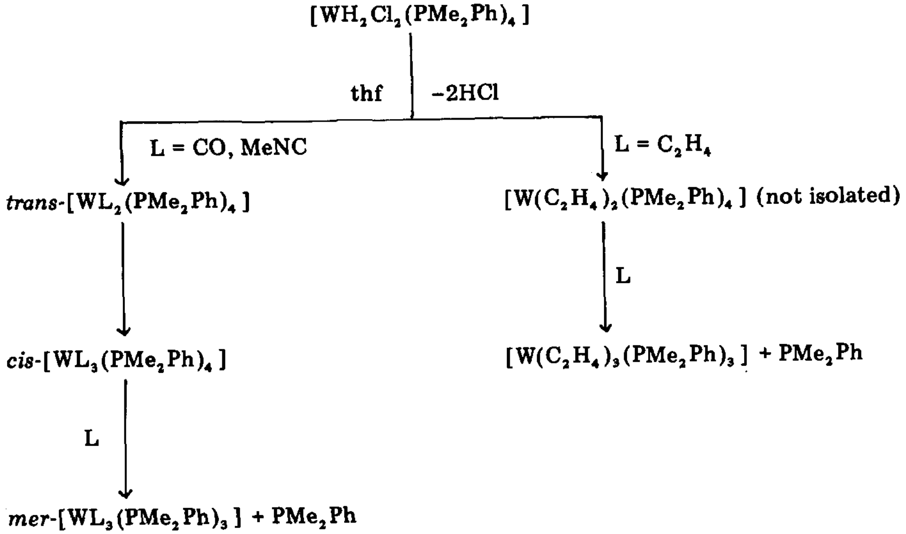
dinating atoms also relates, approximately, the arrangements of the phenyl and methyl groups of the phosphine ligands.

The refined positions of the hydride atoms are considered chemically reasonable and the W—H contacts (1.26(7) and 1.46(5) Å) are not outside the bounds of statistical equivalence. That the W—P(3) and W—P(5) distances are rather shorter than the W—P(4) and W—P(6) distances appears to result from steric effects; the P(3)—W—P(5) angle, 120.8(1)°, is also much smaller than P(4)—W—P(6), 156.8(1)°, reflecting the sizes of the neighbouring hydrido or chloro groups.

The dimensions within the phosphine groups are very similar in the four ligands and are as expected.

Dehydrochlorination of A. Some typical examples of these reactions are shown in Scheme 1. In general, A is stirred with NEt_3 in thf in presence of

SCHEME 1



the ligand (L) and the precipitated $[NEt_3H]Cl$ is filtered before work-up of the product (L = CO, RNC, olefin, N_2 etc.).

The brown complex $[W(C_2H_4)_3(PMe_2Ph)_3]$ has its C_2H_4 resonance at 0.29 ppm (rel. $SiMe_4$, C_6D_6, 25°C). The MeNC products shown in the Scheme have also been obtained from *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ [6], but irradiation and/or heating is necessary to cause dinitrogen loss and the dehydrochlorination reaction is more convenient. The analogues of A, $[MH_2Cl_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo or W) [7], undergo similar reactions to A.

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